

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,113,949

1,113,949



Date of Application and filing Complete Specification: 29 Oct., 1965.
No. 45900/65.

Application made in United States of America (No. 407641) on 30 Oct., 1964.
Complete Specification Published: 15 May, 1968.
© Crown Copyright 1968.

Index at acceptance: —H1 BF
Int. Cl.: —H 01 m 27/00

COMPLETE SPECIFICATION

Improvements in Composite Article and Method of Forming

- We GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, residing at 1 River Road, Schenectady 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to composite articles and to methods of forming composite articles and more particularly to composite articles having a solid oxygen-ion member, and an adherent porous layer thereon of nickel containing an intimate dispersion of solid oxygen-ion material therein, which composite articles are useful as electrode-electrolyte bodies in high temperature fuel cells, and to methods of forming such composite articles.
- Fuel cells, which operate at high temperatures in the range of 1000°C to 1200°C, are advantageous to provide a low voltage direct current power source on a continuous basis.
- These cells have applications in various chemical process industries, such as the manufacture of aluminum and electro-refining copper. Furthermore, these cells can be employed to operate direct current motors.
- It would be desirable to provide an electrode-electrolyte body which is usable in such a high temperature fuel cell. Such a body in the form of a composite article would be advantageous to provide a unitary solid structure incorporating both the electrolyte and the anode which could be readily incorporated into a high temperature fuel cell requiring the employment of a solid electrolyte for its operation. The present invention is directed to such an electrode-electrolyte body.
- The present invention thus provides a composite article comprising a solid oxygen-ion member, and an adherent porous layer on one surface of said member, said layer consisting of at least 50 volume per cent of nickel and the balance being an intimate dispersion of a compatible solid oxygen-ion material, said volume percentages being based upon the total volume of said nickel and said solid oxygen-ion material. Preferably both the said oxygen-ion member and the said compatible oxygen-ion material are of stabilized zirconia or of doped thoria. The said member may be hollow, in the form of a container or in the form of a plate.
- The present invention further provides a fuel cell including a cathode, oxidant supply means for said cathode, and fuel gas supply means for an anode, and a combination of an electrode-electrolyte body, said body comprising a solid oxygen-ion member, and an adherent porous layer on one surface of said member, said layer consisting of at least 50 volume per cent of nickel and the balance being an intimate dispersion of a compatible solid oxygen-ion material, said volume percentages being based upon the total volume of said nickel and said oxygen-ion material.
- The term "solid oxygen-ion conducting electrolyte" means that the electrolyte allows the transfer of oxygen-ions; the term is currently used in the literature on the subject, for example in an article entitled "A Solid Electrolyte Fuel Cell", by J. Weissbart and R. Rulea in the "Journal of the Electrochemical Society" Volume 109, No. 8, page 723 et seq.
- The invention will be better understood from the following description taken in connection with the accompanying drawing in which:

Figure 1 is a sectional view of a composite article embodying the invention;

Figure 2 is a sectional view of a modified composite article;

Figure 3 is a sectional view of another modified composite article; and

Figure 4 is a sectional view of a high tem-

[Price 4s, 6d.]

perature fuel cell embodying the composite article of the invention.

In Figure 1 of the drawing, a composite article is shown generally at 10 which comprises a member 11 of solid oxygen-ion material, and an adherent porous layer 12 on the exterior surface of member 11. For example, member 11 is composed of solid stabilized zirconia and is in the form of a hollow tubular member. Layer 12 consists of at least 50 volume per cent nickel and the balance being of an intimate dispersion of a compatible solid oxygen-ion material. The volume percentages are based upon the total volume of the nickel and the solid oxygen-ion material. The total volume and percentages exclude the porosity of the layer.

In Figure 2, of the drawing, there is shown a modified composite article comprising a container 13 consisting of a solid oxygen-ion material, and an adherent porous layer 14 on the exterior surface of container 13 which layer 14 is of the same material as layer 12 in Figure 1.

In Figure 3 of the drawing, there is shown another modified composite article comprising a plate 15 of solid oxygen-ion material, and an adherent porous layer 16 on one surface of plate 15 which layer 16 is of the same material as layer 12 in Figure 1. In Figures 2 and 3, the container and plate are composed, for example, of solid stabilized zirconia.

In Figure 4 of the drawing, there is shown a high temperature fuel cell 17 embodying composite article 10 of Figure 17 which comprises a hollow tubular member 11 of solid stabilized zirconia, and a porous layer 12 consisting of at least 50 volume per cent nickel and the balance being of an intimate dispersion of a compatible solid oxygen-ion material, such as stabilized zirconia, on the exterior surface of member 11. Member 11 of composite article 10 is the solid electrolyte of fuel cell 17 while porous layer 12 of article 10 is the anode for fuel cell 17. Cathode 18 for fuel cell 17 is composed of a layer of lithiated nickel oxide on the interior surface of electrolyte 11. A conduit 19 surrounds and is spaced from anode 12 to provide a chamber 20.

Electrodes 12 and 18 are reversible i.e. the porous anode 12 may be provided on the interior surface of member 11 and cathode 18 in direct contact with the exterior surface of member 11. A lead 21 of nickel is attached to layer 12 which is the anode while a lead 22 of an oxidation resistant metal or alloy is attached to cathode 18. The free ends of leads 21 and 22 are connected to an electrical load, such as an electric motor, operated by the cell. Means are provided for supplying a gaseous oxidant containing molecular oxygen to cathode 18 which oxidant includes, for example, air or oxygen. An inlet

line 23 connected to an oxidant supply (not shown) supplies oxidant to cathode 18. Inlet line 23 communicates with the aperture defined by cathode 18. An outlet line 24 communicates with the opposite end of the same aperture. A fuel gas, such as hydrogen or carbon monoxide is supplied from a fuel gas source (not shown) through chamber 20 defined between conduit 19 and porous anode 12. The opposite end of conduit 19 removes the effluent material which forms during operation of the cell.

With the above composition, a very desirable anode is formed which adheres well to the electrolyte. The preferred oxygen-ion material in both the electrolyte and anode is solid stabilized zirconia. However, other solid oxygen-ion material such as solid doped thoria is satisfactory in both the electrolyte and anode.

Solid stabilized zirconia, which is a solid oxygen-ion electrolyte material, is a compound with a cubic crystal structure consisting of zirconia to which is added calcium oxide, yttrium oxide, or a mixture of rare earth oxides. For example, a preferred solid zirconia member is employed which is stabilized with 11 molecular per cent calcium oxide.

Solid doped thoria is also a solid oxygen-ion electrolyte material which consists of thoria to which is added calcium oxide, yttrium oxide, or a mixture of rare earth oxides. For example, a solid doped thoria consists of thoria which is doped with the addition of four molecular per cent calcium oxide to increase its conductivity.

It has been found that the above layer of nickel containing an intimate disposition of a compatible solid oxygen-ion material is an electronic conductor which is a very satisfactory anode material employed with a solid oxygen-ion electrolyte.

A preferred method of forming our porous layer consisting of at least 50 volume per cent nickel and the balance being an intimate dispersion of a compatible solid oxygen-ion material, such as stabilized zirconia, on a solid stabilized zirconia member to provide a composite article therefrom is to initially mix lithium carbonate and nickel oxide in proportions to give ten atomic per cent lithium in the metal species (i.e., considering only the total lithium atoms plus the total of the nickel atoms, ten per cent of these atoms are lithium atoms), and grind the lithium carbonate and nickel oxide in an inert vehicle such as ethanol. The resulting mixture is then dried and calcined in air at 1500°C for 30 minutes. The calcined oxide shows a black color typical of metal excess semiconducting compositions based on nickel oxide indicating that a non-stoichiometric compound has formed. The resulting oxide is then crushed, ground, and passed through a 325 mesh

70

75

80

85

90

95

100

105

110

115

120

125

130

screen. The resulting lithiated nickel oxide powder is mixed with an aqueous slurry of stabilized zirconia similar to that of the above electrolyte in a 4:1 ratio by weight. The particle size of the zirconia should be less than 10 microns. It should be noted that the composition of the stabilized zirconia component (present as particles less than ten microns in size) may be somewhat different from the composition of the stabilized zirconia electrolyte so long as the stabilized zirconia component of the anode is still a material which functions as an oxygen-ion conductor. The aqueous slurry of stabilized zirconia can be the so-called "slip" used for fabrication of commercial zirconia bodies by slip casting. This proportion will provide a layer consisting of 70 volume per cent of nickel when the nickel oxide is reduced to nickel. The viscosity of the slip is adjusted by changing its water content.

The slurry is then painted onto the outer surface of a solid stabilized zirconia member such as the hollow tubular member shown in Figure 1 of the drawing. An assembly of the solid stabilized zirconia tubular member with the slurry painted thereon is then dried by infrared heating to remove moisture. The assembly is then fired in air at 1550°C for forty-five minutes, cooled and reheated in hydrogen to 1050°C over a period of about one hour to reduce the nickel oxide to nickel.

The initial air firing of the assembly causes the lithiated nickel oxide to bond to the stabilized zirconia electrolyte and to sinter into a rather dense, strong layer containing an intimate dispersion of zirconia. The subsequent firing of the assembly in hydrogen forms a layer of nickel containing an intimate dispersion of stabilized zirconia, the layer being rendered porous as the result of the volumetric decrease associated with the hydrogen reduction of the nickel oxide to metallic nickel. This layer is bonded to the stabilized zirconia member through a "graded seal" of nickel-zirconia oxide which appears to form when the lithiated nickel oxide is fired on a stabilized zirconia member. The term "graded seal" indicates that at the interface between the anode and the zirconia a transition layer of varying composition occurs extending from the nickel metal (the nickel must be present in greater concentration than the zirconia) to the zirconia electrolyte. The resultant porous nickel layer containing an intimate dispersion of stabilized zirconia is electrically conductive and adheres well to the solid stabilized zirconia member to provide a composite article. The same method may be employed with the zirconia members in Figures 2 and 3 of the drawing. Either the interior or exterior surface of the container in Figure 2 or the plate in Figure 3 is provided with a porous layer of nickel containing stabilized zirconia.

In forming the above porous layer consist-

ing of at least 50 volume per cent nickel and the balance being an intimate dispersion of a solid oxygen-ion material, the nickel metal must be the product of the reduction of lithiated nickel oxide. When lithiated nickel oxide is reduced to nickel metal in accordance with the present method, the resultant porous nickel layer is an electronic conductor. The mixing of similar volume percentages of nickel powder and an oxygen-ion material and sintering of the mixture produces a layer which is not an electronic conductor. Experiments have shown that unless the production of the anode layer is approached via the lithiated nickel oxide-zirconia route, the layer produced will not function as an anode because it does not exhibit electronic conduction.

When we employ lithiated nickel oxide and a solid oxygen-ion material in accordance with the present method we first densify and bond this electrode layer to the electrolyte by sintering thereby eliminating a pressure step during the sintering. This permits formation of the anode layer in various configurations. Additionally, we found that if the anode layer becomes oxidized during operation of the cell, the oxidized portion is converted to lithiated nickel oxide which continues to function as an anode due to its electronic conductivity. The electrical conductivity of this oxide is several orders of magnitude greater than that of pure nickel oxide.

In Figure 4 of the drawing, a hollow tubular member 11 of solid stabilized zirconia with a porous layer 12 thereon of nickel containing an intimate dispersion of solid stabilized zirconia as shown in Figure 1 of the drawing as composite article 10 is prepared as a composite article in accordance with the above method. The composite article which is a unitary electrode-electrolyte body is combined with other elements to form a fuel cell 17. An inlet line 23 is provided to communicate with the aperture defined by the lithiated nickel oxide cathode and to supply an oxidant such as oxygen to cathode 18 of cell 17. An outlet line 24 is provided at the opposite end of the chamber. Conduit 19 supplies a fuel gas such as hydrogen or carbon monoxide to chamber 20 defined thereby to anode 12 while at its opposite end water vapor or carbon dioxide which forms during operation of the cell is removed. A lead 21 of nickel is attached to anode 12 while a lead 22 of an oxidation resistant metal or alloy is attached to cathode 18. The free ends of the leads are connected to apparatus (not shown) being operated by the cell.

In the operation of fuel cell 17 shown in Figure 4, heat, such as waste heat, is supplied from a source (not shown) to raise the temperature of electrolyte 11, anode 12 and cathode 18 to a temperature in the range of 1000°C to 1200°C. The lithiated nickel oxide

70

75

80

85

90

95

100

105

110

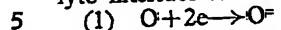
115

120

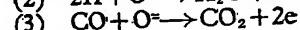
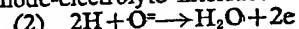
125

130

cathode is then saturated with oxygen which is supplied through inlet line 23 to the cathode. The reaction at the cathode-electrolyte interface is as follows:



The oxygen ion moves through electrolyte 11 to combine with hydrogen in accordance with reaction (2) or to combine with carbon monoxide in accordance with reaction (3) at the anode-electrolyte interface:



The electrons, which are given up at anode 12 are conducted through lead 21 to apparatus (not shown) being operated while the oxygen at the cathode 18 combines with the returning electrons. The water vapor or carbon dioxide which is generated at anode 12 is released to the atmosphere. Such release is through outlet line 24.

20 Composite articles which are unitary electrode-electrolyte bodies were made in accordance with the present invention. These electrode-electrolyte bodies were composite

articles each of which comprised a solid stabilized zirconia member with an adherent porous layer thereon of 70 volume per cent nickel and the balance being an intimate mixture of stabilized zirconia. The porous layer was prepared in accordance with the method set forth above. Two of these composite articles, which are identified by cell numbers 1 and 2 in Table I were tested to determine their effectiveness in high temperature fuel cells each of which employed additionally a lithiated nickel oxide cathode, an oxidant containing molecular oxygen, and a fuel gas of hydrogen which may contain a small amount of oxygen and water vapour. Table I sets forth the cell number, the temperature of operation, the load voltage in volts, and the current density in milliamperes per square centimeter. Each cell was operated for several days. Electrical leads were connected to both electrodes and the power generated by the cell was dissipated in a simple decade resistor. Each cell was heated to its operating temperature in a resistance furnace.

25

30

35

40

45

85

90

95

100

105

Table I

50	Cell No.	Temp. °C	Load Voltage (V)	Current Density (ma/cm²)	
				1	2
	1	1050°C	0.5	50	
	2	1200°C	0.5		260

WHAT WE CLAIM IS:—

- 55 1. A composite article comprising a solid oxygen-ion member, and an adherent porous layer on one surface of said member, said layer consisting of at least 50 volume per cent of nickel and the balance being an intimate dispersion of a compatible solid oxygen-ion material, said volume percentages being based upon the total volume of said nickel and said solid oxygen-ion material.
- 60 2. A composite article according to Claim 1, in which both the said oxygen-ion member and the said compatible oxygen-ion material are of stabilized zirconia.
- 65 3. A composite article according to Claim 1, in which both the said oxygen-ion member and the said compatible oxygen-ion material are of doped thoria.
- 70 4. A composite article according to any one of Claims 1 to 3, in which the said member is hollow.
- 75 5. A composite article according to any one of Claims 1 to 3, in which said member is in the form of a container.
- 80 6. A composition article according to any one of Claims 1 to 3, in which said member is in the form of a plate.

7. A composite article comprising a solid oxygen-ion member with an adherent porous layer constructed and arranged substantially as herein described and shown in any one of Figures 1, 2 and 3 of the accompanying drawings.

8. A fuel cell including a cathode, oxidant supply means for said cathode, and fuel gas supply means for an anode, and a combination of an electrode-electrolyte body, said body comprising a solid oxygen-ion member, and an adherent porous layer on one surface of said member, said layer consisting of at least 50 volume per cent of nickel and the balance being an intimate dispersion of a compatible solid oxygen-ion material, said volume percentages being based upon the total volume of said nickel and said oxygen-ion material.

9. A fuel cell according to Claim 8, in which both the said oxygen-ion member and the said compatible oxygen-ion material are of stabilized zirconia.

10. A fuel cell according to Claim 8, in which both the said oxygen-ion member and the said compatible oxygen-ion material are of doped thoria.

11. A fuel cell comprising a solid oxygen-

ion member and an adherent porous layer constructed and arranged substantially as herein described and shown in Figure 4 of the accompanying diagrammatic drawings.

For the Applicants:—
G. H. MUNSTER & CO.
Chartered Patent Agents
Imperial Buildings, 56, Kingsway,
London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

1113949 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of
 the Original on a reduced scale

Fig.1.

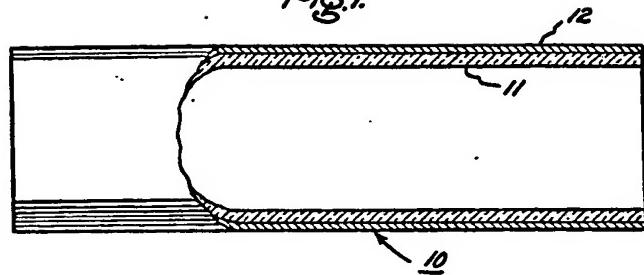


Fig.2.

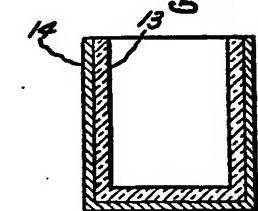


Fig.3.

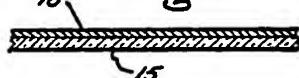


Fig.4.

